ENHANCED PHOTOLUMINESCENCE PROPERTIES OF Mn²⁺ DOPED ZnS NANOPARTICLES

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The room-temperature photoluminescence (PL) of manganese doped zinc sulphide $(ZnS:Mn^{2+})$ nanoparticles have been investigated. These Mn^{2+} doped ZnS nanoparticles have been synthesized by chemical precipitation method at room temperature. It has been found that passivation with acrylic acid (AA) yielded higher photoluminescence intensity. So-prepared Mn^{2+} doped ZnS nanoparticles then characterized by using X-ray diffraction (XRD), Scanning electron microscope (SEM), UV-Vis spectrophotometer. The size of the particle is found to be in 4.59-5.64 nm range. The value of band gap energy has been found to be in range 3.89-4.51 eV. Room temperature photoluminescence (PL) spectrum of the undoped sample exhibit a blue emission peaked at 465 nm under UV excitation whereas the Mn^{2+} doped sample exhibits a yellow emission peaked at 574 nm under same UV excitation.

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1. Introduction

Luminescent semiconductor nano-crystals, especially II–VI semiconductors, have attracted great deal of attention in the past few decades due to their unique properties and potential applications. The most extensively investigated doped semiconductors are Mn doped ZnS or CdS nano-crystals. The doping ions act as recombination centers for the excited electron–hole pairs and result in strong and characteristic luminescence. This II–VI compound semiconductor material has been studied for a variety of applications, such as optical coating, electro-optic modulator, photoconductors, field effect transistors, optical sensors, phosphors, and other light emitting materials. Zinc sulphide doped with transition metal ion is known to have efficient light emitting properties [1]. In doped compound semiconductors, in contrast to the undoped semiconductors, the impurity states can play a special role in affecting the electronic energy structures and transition probabilities [2]. Bhargava et.al. [3] reported that Mn doped nanocrystalline semiconductors yield both high luminescent efficiencies and life time shortening. They have also shown that the quantum efficiency increases with decreasing particle size.

The objective of this work is to study the luminescence characteristics of Mn^{2+} doped ZnS nanoparticles prepared by a surface passivation technique. To achieve the luminescence enhancement, Acrylic acid (AA) is used as a surface passivators after chemical precipitation of Mn^{2+} doped ZnS nanoparticles at room temperature. AA is chosen as a surface passivation legend because it has a carboxylic group in its structure, which has potential to enhance PL. Mn^{2+} ion sites enhance the photoluminescence of the system due to the d-d transition through energy transfer from the S²⁻ vacancies to the AA when excited by UV light [4]. The size of the prepared ZnS and ZnS:Mn nano crystallites are calculated and it is found in the range of 4.59-5.64 nm. The PL emission takes place in the yellow region for Mn doped ZnS sample with a peak at 574 nm whereas the undoped ZnS sample emits in the blue region.

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2. Experimental

2.1. Sample Preparation

The important step in the studies of nanoparticle is their synthesis. We have used here chemical precipitation method to synthesize the samples at room temperature using $Zn(CH_3COO)_2.2H_2O$, $Mn(CH_3COO)_2.4H_2O$, and $Na_2S.9H_2O$ as source materials. The chemical precipitation method is the most popular technique because of its several advantages like easy handeling, simpler and with low-cost chemical compounds and it is suitable for industrial large scale production [5]. We prepare 50 ml solution by mixing 2.195gm $Zn(CH_3COO)_2.2H_2O$ and 0.049gm. $Mn(CH_3COO)_2.4H_2O$ with stirring at room temperature for 15 min. Then 50 ml aqueous solution of 2.451 gm $Na_2S.9H_2O$ has been added to the earlier solution drop by drop and mixed for 25 min with vigorous stirring resulting dull white colloidal solution. After that appropriate amounts of acrylic acid are added and mixed for 20 min. The powder sample was then separated from the solvent and washed with methanol several times, after wash it is oven dried for 24 hours at 50°C. After drying the precipitate it is crushed in to fine powder with the help of mortar and pestle. The powder obtained is then characterized.

2.2. Characterization techniques

The size of all the samples are determined by Phillips Expert Pro X-ray diffractometer with CuK α radiation (λ =0.150406nm). XRD data are collected over the range 20⁰ – 80⁰ at room temperature. The particle size is calculated by using the Scherrer formula. The morphology of the nanoparticles is determined using scanning electron microscopy (FESEM; QUANTA 3D FEG). Absorption spectra of the samples dispersed in methanol are studied with the help of U-3010 Spectrophotometer. The PL spectrum of the ZnS and ZnS:Mn nanoparticle has been measured at room temperature using Hitachi F-2500FL Spectrophotometer.

3. Results and discussion

3.1. X-ray diffraction pattern

The XRD patterns of ZnS:Mn nanoparticle samples are shown in Fig. 1. The crystalline size can be calculated with the help of Scherrer's equation mention below

$$D = \frac{0.9\lambda}{\beta\cos\theta} \tag{1}$$

Where D is the mean grain size, λ is the X-ray wavelength (for CuK α radiation, $\lambda = 0.15406$ nm), θ is the diffraction angle and β is full width at half maximum. The grain size of the undoped ZnS and 2% Mn doped ZnS nanoparticle as calculated by using Eq.(1) is in range of 4.59 - 5.64 nm. Figure 1 shows the three diffraction peaks at 2θ values equal to 28.7°, 47.6° and 56.5° which appears due to reflection from the (111), (220) and (311) planes of the cubic phase of the ZnS. The obtained peak positions correspond to zinc blended type patterns for all the samples. The XRD pattern of the nanocrystal is well matched with the Standard cubic ZnS [6]. The broadening of the XRD pattern of the prepared ZnS:Mn sample takes place due to the nanocrystalline nature of the sample. In this investigation we found that with increasing amount of AA particle size is decreasing as shown in Table - I.



Fig. 1. XRD pattern of ZnS and ZnS:Mn nanoparticle.

3.2. SEM analyses

Fig. 2 shows the FESEM image of the undoped ZnS and 2% Mn doped ZnS nanoparticles. The actual size of the nanoparticle can not be determined from the FESEM images as it is limited by the resolution of the used FESEM instrument.



Fig. 2. FESEM image of (a) undoped ZnS, (b) 2% Mn doped ZnS, (c) 2% Mn doped ZnS with 0.1 mol AA, (d) 2% Mn doped ZnS with 0.5mol AA and (e) 2% Mn doped ZnS with 0.75 mol AA.

3.3. Optical absorption and band gap

The optical absorption spectra have been observed by using Hitachi U-3010 UV-Visible spectrophotometer and the results are shown in Fig. 3. To measure the absorption characteristics, the synthesized ZnS nanopowders are first dispersed in methanol and then taken on a quartz

cuvette. From the optical absorption spectera of Mn^{2+} doped ZnS nanoparticles it is clear that with increasing acrylic acid peak shifts towards shorter wavelength. Optical absorption spectera of Mn^{2+} doped ZnS nanoparticles shows that the peak appears in the range of 350-250 nm. These peak positions reflect the band gap of nanoparticles and the synthesis ZnS nanoparticles have no absorption in the visible region (800-400nm). The relation between the incident photon energy (*hv*) and the absorption coefficient (α) is given by the following relation

$$(\alpha h \nu)^{\frac{1}{n}} = A(h\nu - E_g)$$
⁽²⁾

Where A is constant and E_g is the band gap energy of the material and the exponent n depends on the type of transition. For direct allowed transition n = 1/2, for indirect allowed transition n = 2, for direct forbidden n = 3/2 and for indirect forbidden n = 3. Direct band gap of the samples are calculated by plotting $(\alpha hv)^2$ verses hv and then extrapolating the straight portion of the curve on hv axis at $\alpha = 0$ as shown in Fig. 4. The band gap energy of the samples is found in the range 3.89 -4.51 eV as indicated in Table- I. The obtained values of the band gap of ZnS and Mn doped ZnS nanoparticles are higher than that of the bulk value of ZnS (3.68 eV). This blue shift of the band gap takes place because of the quantum confinement effect [3].



Fig. 3. Absorption spectrum of ZnS and Mn^{2+} doped ZnS nanoparticles.



Fig. 4. Calculation of optical band gap from the UV-Vis absorption spectra.

Table-I: Particle size and corresponding band gap energy of the synthesis nanomaterials.

Sample Name	Particle size (nm)	Band gap energy (eV)
Undoped ZnS	5.64	4.51
2% Mn doped ZnS	5.52	3.89
2% Mn doped ZnS with 0.1 mol AA	5.08	3.97
2% Mn doped ZnS with 0.5 mol AA	4.65	4.01
2% Mn doped ZnS with 0.75 mol	4.59	4.27
AA		

3.4 Photoluminescence study of ZnS:Mn²⁺ nanoparticles

Photoluminescence (PL) of the ZnS:Mn samples are measured at room temperature using F-2500FL Spectrophotometer. The PL spectrum of Mn²⁺ doped ZnS nanoparticles are shown in Fig. 5. The PL spectrum shows the efficient emission of yellow color light with peak at 574 nm due to the excitation wavelength of 260 nm. Whereas the undoped ZnS sample shows the blue emission. The doping of Mn²⁺ in host ZnS produce energy levels between the conduction band and valence band of the ZnS, leads to the emission of yellow colour light from Mn²⁺ doped ZnS nanoparticle. Lu et al. [7] reported that the PL intensity of Mn²⁺ doped ZnS nanocrystals passivated by MPTS was enhanced by a 30-fold, in comparison with the samples without MPTS passivation. ZnS:Mn nanocrystals are found to have increased photoluminescence efficiency with a very short lifetime of the transition associated with the magnetic impurity Mn²⁺ [8]. For small particles like the $ZnS:Mn^{2+}$ nanoparticles, majority of the Mn^{2+} ions are at the near-surface sites and occupy axial or lower symmetry sites [9]. The PL spectrum shows that the addition of AA enhances the PL intensities in comparison of the sample without addition of AA. This is due to the reduction of surface defects. The yellow emission originates from a transition between the ${}^{4}T_{1}$ excited state and ${}^{6}A_{1}$ ground state of Mn²⁺ ion. The PL enhancement can be explained by a passivation of the surface defects on nanoparticle. Non-radiative recombination occurs through surface defects, the radiative probability through the Mn²⁺ centres decreases with increasing surface defects. So it is expected that an enhancement of the radiative probability will be obtained by elimination of the surface defects through surface passivation. In the presence of AA as a surface passivator the surface defects on Mn^{2+} doped ZnS nanoparticles are passivated and eliminated. The carboxylic groups of surface modifying agents play an important role in enhancing the PL intensity [7].



Fig. 5. PL emission spectrum of the ZnS and ZnS:Mn nanoparticles.

4. Conclusions

Manganese doped zinc sulphide (ZnS: Mn^{2+}) nanoparticles are prepared using acrylic acid as a surface passivator by chemical method at room temperature. The XRD measurements yielded the particle size in the range of 4.59 - 5.64 nm. It has been observed that with the increasing acrylic acid concentration the absorption peak of the Zns:Mn shifts towards shorter wavelength. The band gap energy of the samples is found in the range 3.89-4.51eV. Room temperature photoluminescence (PL) spectrum of the undoped sample exhibit a blue emission peaked at 465 nm under UV excitation whereas the Mn^{2+} doped sample exhibits a yellow emission peaked at 574 nm under same UV excitation. The enhanced PL intensity is due to AA, this is achieved by eliminating the surface defects, in which the carboxylic group present in surface passivator plays an important role.

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